

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets

(11)

Publication number:

0 170 895**A2**

(12)

EUROPEAN PATENT APPLICATION

(21)

Application number: 85108378.2

(51)

Int. Cl.: **B 01 D 13/02, C 02 F 1/46,**
B 01 J 47/08

(22)

Date of filing: 05.07.85

(30)

Priority: 09.07.84 US 628930

(71)

Applicant: **MILLIPORE CORPORATION, 80 Ashby Road,**
Bedford Massachusetts 01730 (US)

(43)

Date of publication of application: 12.02.86
Bulletin 86/7

(72)

Inventor: **Gluffrida, Anthony J., 254 Chestnut Street, N.**
Andover, MA 01845 (US)
Inventor: **Jha, Anil D., 13 Sheridan Street, Lexington,**
MA 02173 (US)
Inventor: **Ganzl, Gary C., 74 Valleyfield Road, Lexington,**
MA 02173 (US)

(84)

Designated Contracting States: **CH DE FR GB LI NL SE**

(74)

Representative: **Henkel, Feller, Hänzeli & Partner,**
Möhlstrasse 37, D-8000 München 80 (DE)

(54)

Improved electrodeionization apparatus and method.

(57)

An electrodeionization apparatus and process are provided for removing ions from liquids. Liquid to be purified is passed through depleting compartments containing mixed anion and cation exchange resin beads while a second liquid is passed through concentrating compartments free of ion exchange resin beads. Ions, under influence of a D.C. potential, pass from the depleting compartments into the concentrating compartments through ion permeable membranes. The beads in the depleting compartments are housed within subcompartments of controlled width and thickness and are retained therein by the ion permeable membranes which are secured to the walls of the subcompartments.

EP 0 170 895 A2

Improved Electrodeionization Apparatus and MethodBackground of the invention

This invention relates to a novel electrodeionization apparatus and method adapted to transfer ions in a liquid under the influence of a polar field. More specifically, this invention relates to an electrodeionization apparatus and method adapted to purify aqueous liquids to effect the production of high purity water.

The purification of a liquid by reducing the concentration of ions or molecules in the liquid has been an area of substantial technological interest. Many techniques have been used to purify and isolate liquids or to obtain concentrated pools of specific ions or molecules from a liquid mixture. The most well known processes include electrodialysis, liquid chromatography, membrane filtration and ion exchange. A lesser known methodology is electrodeionization, occasionally mislabeled filled cell electrodialysis. Although electrodeionization has the potential to be quite effective in removing ions from liquid, it has never been developed to the degree that it is competitive either structurally or operationally with the better known separation techniques. This is due primarily to the inconsistencies of structural design and unpredictable variances incurred by the presently known modes of use. This lack of structural design precision and nonpredictability of results have reduced the use of electrodeionization to the point where it is relatively unknown even to practitioners skilled in separation methodologies.

The first apparatus and method for treating liquids by electrodeionization was described by Kollsman in U.S.

Patent Nos. 2,689,826 and 2,815,320. The first of these patents describes an apparatus and process for the removal of ions within a liquid mixture in a depleting chamber through a series of anionic and cationic diaphragms into a second volume of liquid in a concentration chamber under the influence of an electrical potential which causes the preselected ions to travel in a predetermined direction. The volume of the liquid being treated is depleted of ions while the volume of the second liquid becomes enriched with the transferred ions and carries them in concentrated form. The second of these patents describes the use of macroporous beads formed of ion exchange resins as a filler material positioned between the anionic or cationic diaphragms. This ion exchange resin acts as a path for ion transfer and also serves as an increased conductivity bridge between the membranes for the movement of ions. These patents represent the primary structural framework and theory of electrodeionization as a technique. The term electrodeionization refers to the process wherein an ion exchange material is positioned between the anionic and cationic diaphragms. The term electrodialysis relates to such a process which does not utilize ion exchange resins between the anionic and cationic diaphragms. Despite the fact that the Kollsman technique has been available for over 25 years, this technology has not been developed even to the point of practical use. This is due in no small part to the lack of structural designs and the unavailability of operational mode parameters which afford reliable operation of the electrodeionization apparatus. Illustrative of prior art attempts to use the combination of electrodialysis and ion exchange materials to resins to purify saline from brackish water are described in U.S. Patent Nos. 2,794,777; 2,796,395; 2,947,688; 3,384,568 and 4,165,273. Attempts to improve

electrodeionization apparatus are shown in U.S. Patent Nos. 3,149,061; 3,291,713; 3,515,664; 3,562,139; 3,993,517 and 4,284,492.

5 Despite the contributions of the prior art, no reliable
electrodeionization apparatus has been produced. The
typical resin fouling and membrane scaling problems of
electrodeionization remain unalleviated. Presently
described electrodeionization apparatus remain unsuitable
10 for desalination or for the production of high purity
water. Hard waters, silica-containing waters and highly
saline brackish waters, and waters containing colloidal
particles and foulants still represent liquids that
cannot be consistently and reliably purified by presently
15 known electrodeionization apparatus and modes of
operation. Extensive maintenance and cleaning of these
apparatus remain necessary, the quality and volume of the
purified liquids remain erratic and the ability to
produce at least 1 meg-ohm centimeter quality water
20 consistently and in sufficient volume remain unachieved.

Accordingly, it would be desirable to provide a method
and apparatus utilizing electrodeionization capable of
producing a high purity deionized water over long periods
25 of time without the need for shutting down the apparatus
either because of reduction of ion exchange resin
performance or because of particle or scale build-up.
Furthermore, it would be desirable to provide such a
method and apparatus which can be operated efficiently
30 with low energy requirements and high liquid throughput.

Summary of the invention

The present invention provides a method and apparatus capable of continuously producing water of up to about 10
5 meg-ohm cm quality or higher over long periods of time while avoiding serious reduction of ion exchange resin performance and avoiding the build-up of particulates and scale within the electrodeionization apparatus. The apparatus includes a plurality of electrodeionization
10 compartments whose thickness, width and configuration are controlled and which contain ion exchange materials such as beads, fibers or the like. The electrodeionization ion depleting compartments wherein liquid is depleted of ions are formed from a spacer having a hollow central
15 portion divided by ribs or the like to define subcompartments. The ion exchange resin beads within the subcompartments are retained in the subcompartments by bonding or physically restraining a cationic permeable membrane to one surface of the depleting compartments and to the
20 ribs and bonding or physically restraining an anionic permeable membrane to the opposing surface of the depleting compartment to the ribs, thereby to define the subcompartments. The concentration compartments into which ions migrate from the depleting compartments are
25 free of ion exchange beads. The electrodeionization apparatus can comprise a single stage or a plurality of stages in series wherein the process voltage can be controlled independently in each stage, if desired.

30 Brief description of the drawings

Figure 1 is an exploded view of a multistage electrodeionization apparatus of this invention.

Figure 2 is a schematic view illustrating the operation of the apparatus of this invention.

Figure 3 is a pictorial view of a closing mechanism
5 useful in the apparatus of this invention.

Figure 4 is a pictorial view of an electrode structure useful in the apparatus of this invention.

10 Figure 5 is a pictorial view of a spacer construction positioned adjacent an electrode of the apparatus of this invention.

Figure 6 is a pictorial view of a flexible spacer construction which includes the concentration chambers of
15 the apparatus of this invention.

Figure 7 is a pictorial view showing the depletion chambers of the apparatus of this invention.
20

Figure 8 is a detailed view of the liquid inlet means to the structure of Figure 7.

Figure 9 is a pictorial view of an interior electrode assembly utilized in the plural stage embodiment of the
25 apparatus of this invention.

Figure 10 is a schematic diagram showing possible liquid flow paths of electrode stream flows between electrical
30 stages of this invention.

Figure 11 is a schematic diagram showing possible liquid flow paths for depletion and concentration compartments for each electrical stage.

Detailed description of specific embodiments

In accordance with this invention, an electrodeionization apparatus is provided wherein each electrodeionization electrical stage includes an anode and a cathode, and their compartments, a series of concentration compartments which include means for causing turbulent flow of liquid passing therethrough and a series of depletion compartments that contain an ion exchange material such as a mixture of anion exchange resin and cation exchange resin. The depletion compartments are formed so that the ion exchange resin mixture is housed within independent discrete subcompartments each of which has a width of about four inches or less, preferably between about 0.5 and about 1.5 inches. The discrete subcompartments are formed by securing, such as by bonding, both the anion permeable membrane and the cation permeable membrane to the periphery of the depletion compartment and to ribs which extend across the thickness of and along the entire length of the depletion compartment so that each subcompartment is defined by a pair of ribs, the anion permeable exchange membrane and the cation permeable membrane. It has been found, in accordance with this invention that the thickness and width of the depletion compartments are critical to achieving efficient operation of the electrodeionization apparatus. The solid ion exchange material positioned within the subcompartments are constrained from moving between subcompartments by the ribs and ion permeable membranes. Representative suitable solid ion exchange materials include fibers or beads or the like. When employing ion exchange beads, typical bead diameter is about .04 inches or less, preferably between about .033 and about .012

inches in diameter (20 to 50 mesh).

The electrodeionization apparatus can comprise one or a plurality of stages. In each stage, an anode is positioned at an opposite end of a stack of depleting and concentrating compartments from an end at which a cathode is positioned. Each anode and cathode is provided with an adjacent electrode spacer and an ion permeable membrane wherein an electrolyte passes through the electrode spacer. The remaining portion of each stage comprises a series of alternating depletion and concentrating compartments constructed as set forth herein. The liquid to be depleted of ions can be passed in parallel through each depleting compartment in each stage and a second liquid can be passed through each concentrating compartment in parallel in each stage in order to effect removal of ions from the first liquid in the depleting compartments into the second liquid in the concentrating compartments. When a plurality of stages are utilized, the liquid removed from the depleting compartments in an upstream stage can be directed in series into the depleting compartments in the next adjacent downstream stage. Similarly, the liquid removed from the concentrating compartments of an upstream stage can be directed in series to the concentrating compartments in the next adjacent downstream stage. Electrolyte can be passed through the spacer adjacent each electrode in the electrodeionization apparatus and is removed from the electrodeionization apparatus. Other possible liquid flow arrangements will be discussed in detail with reference to Figures 10 and 11.

As stated above it is essential that the subcompartments in the depleting compartments have a controlled thickness

and width in order to sustain high efficiency for ion depletion over long periods. The thickness of the subcompartment should be between about 0.25 and about 0.05 inches, preferably between about .06 and .125 inches. The width of the subcompartment should be between about 0.3 and about 4 inches, preferably between about .5 and about 1.5 inches. There is no limit on the length of the compartment other than as dictated by practical construction and fluid pressure loss considerations. Obviously, the longer the subcompartment length, the greater the ion removal from the liquid therein. Generally, the length of the subcompartments are between about 5 inches and about 70 inches. The subcompartments can contain 100% anion exchange material, 100% cation exchange material or a mixture of the two. When it is desired to remove only a particular anion or particular cation, 100% of the appropriate ion exchange material is used. Usually it is desired to remove both cations and anions in order to produce a purified liquid product. When utilizing strong acid-base resin materials such as beads, the ratio of anion exchange resin beads to cation exchange resin beads generally are about 60 to 40 by volume. By utilizing the subcompartment structure in the depleting compartments, efficient mixing of the liquid and the beads therein is attained while avoiding channeling of the liquid through the depleting compartments as well as avoiding compaction or movement of the beads within a portion of the volume of the depleting compartment. Thus, efficient interchange of the ions and the liquid in the depleting compartment with the ions in the beads to effect ion removal from the liquid in the depleting compartment is attained. Furthermore, it has been found that by controlling the geometry of the subcompartments as set forth herein, relatively low energy requirements for the

electrodeionization apparatus can be utilized even over long periods to attain desired liquid purity.

This invention will now be described with reference to the accompanying drawings. A multistage electrodeion-
5 ization apparatus is shown in Figure 1.

Referring to Figure 1, the electrodeionization apparatus 10 comprises a first stage 12 and a second stage 14. The first stage 12 includes an end plate 13 having an expand-
10 able bladder 15 and an inlet 16 for fluid to expand the bladder 15. Adjacent the endplate 13 is an endblock 17 to house electrode 9 and provide desired manifolding. An electrode spacer 18 is positioned adjacent to the end
15 block 17 and includes a screen 19 which effects turbulent flow of liquid passing through the electrode spacer 18. An ion permeable membrane 20 is sealed to the periphery
20 21 of electrode spacer 18. A spacer 22 formed of flexible material includes a screen 24. The spacer 22 and screen 24 comprise the concentrating compartment of the electrodeionization apparatus of this invention. The
25 depleting compartment structure of this invention comprises an ion permeable membrane 26, a spacer formed of rigid material 28 and an ion permeable membrane 30. The
30 ion permeable membranes 26 and 30 are sealed to the periphery 32 of the spacer 28 on opposite surfaces of the spacer 28. Mixed ion exchange resin beads 34 are housed within a central space which includes ribs (not shown) and are retained therein by the membranes 26 and 30. The
35 unit which comprises spacers 22 and 28 and membranes 26 and 30 are repeated usually between about 5 and about 100 times in order to provide reasonable liquid flow through capacity in stage 12. A spacer 38 formed of flexible material and ion exchange membrane 40 sealed to the
periphery of spacer 38 forms the end concentrating

compartment. An electrode spacer 42 is positioned adjacent the middle block 44 and end electrode 46.

Stage 14 is identical in structure to stage 12 but can have more or fewer cell pairs and includes electrode spacer 48 and membrane 50 attached to the periphery of electrode spacer 48. An electrode 52 is provided in middle block 44. The repeating unit in stage 14 comprises a spacer 54 formed of flexible material as well as a spacer 56 formed of rigid material to which are secured such as by bonding or by mechanical means membranes 58 and 60. A spacer 61 formed of flexible material then is provided followed by a membrane 63, an electrode spacer 65, and endblock 66 and electrode 67, an end plate 68 and a flexible bladder 70 which is inflated by means of fluid passing through conduit 72. Flowthrough of liquid in the concentrating and depleting compartments as well as in the electrode compartment will be explained with reference to the remaining figures. The electrodeionization apparatus is retained in place by bolts 73 and 74 as well as by bolts on the opposing end of the apparatus 10 that extend along the entire length of the apparatus 10. The number of repeating units in the second stage 14 is usually about 5 and about 100, preferably between about 20 and about 60.

By independently varying voltage, electrical current can be controlled in each stage to provide good economy and efficiency for the overall electrodeionization process. Alternatively, a single stage 14 can be utilized as the apparatus of this invention or additional stages can also be utilized. In any event, the flow rate of liquid through the depleting and concentrating compartments and the operating voltage utilized in a particular stage is controlled to maximize efficiency for

the overall apparatus in terms of ion removal and electrical power utilized.

Referring to Figure 2, the flowpaths of the liquids in the various compartment are explained. Liquid to be purified enters inlet 75, passes through depletion compartments 28, is then passed through depletion compartments 56 and is recovered from outlet 77. Concentrating liquid is passed through outlet 79 through concentrating compartments 22 and 54 and thence through outlet 81 to drain. Liquid electrolyte is circulated through electrode compartments 19, 46, 52 and 67 from inlets 82 and is discarded to drain through outlets 78.

Referring to Figure 3, the end plate 13 includes a bladder 15 and conduit 16 through which fluid can enter in order to expand bladder 15. Bolt holes are provided around the periphery of the end plate in order to pass bolts thereto and to secure the entire apparatus during use.

Referring to Figure 4, the electrode structure is shown which comprises a rigid block 66 and an electrode 67. The end block 66 is provided with electrolyte feed inlet 82 and electrolyte waste outlet 78. Electrode 67 includes a connector 85 which contacts the exterior electrical connection 87 as shown in the detail portion of Figure 4. The block 66 includes an inlet 75 and outlet 77 for depletion compartments and inlet 79 and outlet 81 for concentration compartments.

Referring to Figure 5, the electrode spacer 65 includes electrolyte inlet 82 and electrolyte outlet 78 and a screen 90 for effecting turbulence of liquid passing therethrough.

Referring to Figure 6, the spacer formed of flexible material, e.g. spacer 38, includes a liquid inlet 79 and a liquid outlet 81 which provide liquid communication to the interior of spacer 38 in which is positioned a screen
5 95 in order to effect turbulent liquid flow. The outlet 99 permits passage of liquid into the adjacent depleting compartments and inlet 97 permits liquid removal from the adjacent depleting compartment without admixture of the purified liquid with the liquid in the concentrating
10 compartment formed in spacer 38.

Referring to Figures 7 and 8, the structure of the depleting compartments of this invention is shown in detail. The depleting compartment comprises a rigid
15 spacer, e.g. spacer 28, and an anion permeable membrane 30 and cation permeable membrane 26. The ion exchange materials 34 are housed within subcompartments formed by the membranes 26 and 30, the wall 105 and the ribs 99. The membranes 26 and 30 are sealed along their entire
20 length to wall 105 and ribs 99. The membranes 26 and 30 are also sealed to the periphery of the rigid spacer 28 so that the individual subcompartment 98 are effectively isolated from each other. Liquid to be purified enters inlet 75, passes along conduit 100, through inlets 101
25 and into the subcompartments 98 wherein they are subjected to an electrical voltage in order to pass anions through membrane 30 and cations through membrane 26. The purified liquid then passes through outlets 102 and spacer outlet 77 wherein it is collected in
30 accordance with the explanation of Figure 2.

Referring to Figure 9, the middle electrode block 44 includes electrodes 52 and 46 each having electrical connectors 85 and 87 as shown in Figure 4. The con-
35 nection for electrode 46 is not shown in Figure 9 but is

positioned on the wall 104 in the same manner as shown for electrode 52. Inlet 108 is provided for electrolyte for electrode 46 and outlet 107 is provided for waste electrolyte utilized with electrode 52. The same arrangement is provided on wall 104 for the electrolyte inlet and outlet (not shown).

Figure 10, is a schematic illustration of various flows of the electrode streams of an electrodeionization apparatus assuming two electrical stages. In embodiment (a), inlet liquid is passed into each electrode compartment and removed therefrom in parallel. In embodiment (b), inlet liquid is passed into each anode compartment; removed therefrom, passed to the cathode compartment in the same electrical stage and removed from the apparatus. In embodiment (c), inlet liquid is passed into an anode compartment of the first stage, directed to an anode compartment in a second electrical stage, passed to the cathode compartment of the second electrical stage, passed to the cathode compartment of the first electrical stage and then removed from the apparatus. In embodiment (d) liquid is passed in parallel to the anode compartment and cathode compartment of a second electrical stage. Liquid from the cathode compartment is removed from the apparatus while liquid removed from the anode compartment is passed sequentially to the anode compartment and cathode compartment of an adjacent electrical stage. In embodiment (e) liquid is passed sequentially to the anode compartment of a first stage, the anode compartment of a second stage, the cathode compartment of the second stage and removed from the aperture. A second liquid stream product from a first stage depleting compartment is passed through the cathode compartment of the second stage.

Figure 11 is a schematic illustration of various flow configurations of depleting and concentrating compartments assuming two electrical stages. In embodiment (a) of Figure 11 two liquid streams are
5 cocurrently passed in parallel; one to all the depletion compartments sequentially and the other through the concentration compartments sequentially. In embodiment (b) the liquid stream are flowed as in embodiment (a) except that they are flowed countercurrently. In embodiment
10 ment (c) a portion of the depletion stream from the first stage is cycled into the concentration stream and flowed countercurrent through the concentration compartments sequentially. In embodiment (d) a portion of the depletion stream from the first stage exiting from
15 alternating depletion compartments are passed directly to the concentration compartment of a second stage concentration compartment. The first stage concentrating compartment is fed from the original feed. In embodiment (e) the depleting compartments are fed concurrently while
20 the first and second stage concentrating compartments are fed separately from the original feed.

In one aspect of this invention, the apparatus is operated periodically during the process under conditions to
25 polarize water in the depleting compartments therein to form hydrogen and hydroxyl ions. Generally, operating voltage above about 1.5 volts/cell pair will effect water polarization. The hydrogen ions are selectively removed from the depletion compartments through the cation perme-
30 able membranes thereby to decrease the pH of the water in the concentrating compartment to about 5 or less. By operating in this manner any scale formed in the concentration compartments is dissolved. The low pH effluent from the anode compartment then can be directed to the
35 cathode-compartment in order to dissolve any scale formed

therein. During this step product from the depletion compartments is discarded because of its elevated pH. The effluent from the electrode compartments formed during the scale removal step is discarded. Normal
5 operating voltages then are resumed and the product from the depletion compartments is recovered.

In another aspect of this invention, the apparatus can be backwashed to remove small particles retained within the
10 apparatus, particularly within the depletion compartments. Since the inlets to the subcompartments are smaller than the size of the ion exchange materials therein, only the smaller particles are removed therefrom during backwashing. Backwashing merely comprises passing
15 cleansing liquid into the apparatus through the normally used liquid outlet(s) and removing the cleansing liquid through the normally used liquid inlet(s).

In a third aspect of this invention, the liquid to be
20 purified can be pretreated prior to electrodeionization to remove specific contaminants such as organics. A softener-scavenger system can be employed wherein the softener can include a cation exchange resin and/or an anion exchange resin to remove specific ions. The
25 scavenger can comprise an anion exchange resin in order to remove foulants that foul the anion resin such as organics including tannins and malignans, humic acid, fulvic acids and lignins. The ion exchange resins can be regenerated with brine (NaCl) efficiently and simply.

30 Any anion permeable membrane or cation permeable membrane having the strength to withstand the operating pressure differential, typically up to about 5 psi, can be utilized in the present invention. It should be pointed
35 out that sealing of the membranes to the ribs forming the subcompartments permits the use of higher operating pressures and enhances the apparatus of the prior art

since the assembly strength is thereby increased. Representative suitable anion permeable membranes include a homogeneous type web supported styrene - divinylbenzene based with sulfonic acid or quarternary ammonium functional groups sold under the identifications CR61-CZL-386 and AR 103-QZL-386 by Ionics Inc.; a heterogeneous type web supported using styrene - divinylbenzene based resins in a polyvinylidene fluoride binder sold under the identifications MC - 3470 and MA - 3475 by Sybron/Ionac; homogeneous type unsupported - sulfonated styrene and quaternized vinylbenzylamine grafts of polyethylene sheet sold under the name, Raipore by RAI Research Corporation; a homogeneous type web supported styrene - divinylbenzene based with sulfonic acid or quaternary ammonium functional groups sold under the name Neosepta by Tokuyama Soda Co. Ltd.; a homogeneous type web supported styrene - divinylbenzene based with sulfonic acid or quaternary ammonium functional groups sold under the name Aciplex by Asahi Chemical Industry Co. Ltd.

The process of this invention can be controlled by measuring product water conductivity from all or any one of the stages and adjusting the process parameters including process voltage, liquid flow velocities, temperatures, pressures, and electrical current accordingly.

The following is a description of two methods for controlling the demineralization of an electrodeionization system. The methods can be used separately or in combination in a single or multi-electrical staged system. The first method senses the resistivity and temperature of the feed water and the appropriate cell pair voltage is applied to demineralize the liquid to the desired fraction salt removal.

The second method senses the product resistivity and temperature that is used to control the voltage of the stage to produce water of the desired quality. This type of voltage control can be used to provide product water
5 of a pre-selected quality.

An example of a two-stage system is as follows: The first stage is operated at a variable voltage based on the feed water quality (about 0.5 to 2.0 volts per cell
10 pair) appropriate to achieve approximately 70-80 percent salt removal by using a predetermined resistivity/temperature/percent salt removal relationship. The automatically applied voltage permits operation below the polarization point, thus assuring effi-
15 cient operation without scaling. The second stage is operated at a variable voltage based on the product water quality (about 0.5 to 2.0 volts per cell pair), appropriate to provide water of a pre-selected quality. Since the feed water to the second stage is product water from
20 the first, the second stage feed is less prone to scaling. For this reason polarization in the second stage is acceptable, and the voltage can therefore be varied to any degree to provide the required product quality.

Claims

1. Electrodeionization apparatus adapted to remove ions from a liquid which comprises:

a cathode compartment at a first end of said apparatus,

5 an anode compartment at an end of said apparatus opposite said first end,

a plurality of alternating ion depletion compartments and ion concentration compartments positioned between said cathode compartment and said
10 anode compartment,

each of said ion depletion compartments comprising a plurality of subcompartments containing an ion exchange solid composition each of said subcompartments having a width between about .3 and 4 inches and a thickness
15 between about .05 and .25 inches and wherein the thickness of said subcompartments is defined by an anion permeable membrane and a cation permeable membrane,

each of said concentration compartments being free of ion exchange solid composition,

20 means for passing a first liquid to be purified through said ion depletion compartments,

means for passing a second liquid for accepting ions from said first liquid, through said concentration compartments,

25 means for applying an electrical voltage between an anode in said anode compartment and a cathode in said cathode compartment and,

means for recovering purified liquid from said depletion compartment.

2. The apparatus of claim 1 wherein the width of said subcompartment is between about .5 and 1.5 inches.

3. The apparatus of claim 1 wherein the thickness
5 of said subcompartment is between about .06 and .125 inches.

4. The apparatus of any one of claims 1, 2 or 3 which includes means in said concentration compartments
10 for effecting turbulent flow of said second liquid.

5. The apparatus of any one of claims 1, 2 or 3 wherein the ion exchange material comprises a mixture of anion exchange resin beads and cation exchange resin
15 beads and wherein the volume ratio of anion exchange resin beads to cation exchange resin beads in said ion depletion compartments is between about 2.0 and 0.5.

6. Electrodeionization apparatus adapted to remove ions from a liquid which comprises a plurality of stages, each stage comprising:

5 a cathode compartment at a first end of said apparatus,

an anode compartment at an end of said apparatus opposite said first end,

10 a plurality of alternating ion depletion compartments and ion concentration compartments positioned between said cathode compartment and said anode compartment to define a first stage,

15 each of said ion depletion compartments comprising a plurality of subcompartments containing an ion exchange solid composition, each of said subcompartments having a width between about .3 and 4 inches and a thickness between about .05 and .25 inches and wherein the thickness of said subcompartments is defined by an anion permeable membrane and a cation permeable membrane,

20 each of said concentration compartments being free of ion exchange resin solid composition,

means for passing a first liquid to be purified through said ion depletion compartments,

25 means for passing a second liquid for accepting ions from said first liquid, through into said concentration compartments

means for applying an electrical voltage between an anode in said anode compartment and a cathode in said cathode compartment,

means for transferring purified liquid from the depletion compartments of the first stage to a next adjacent downstream stage,

means for transferring said second liquid from the
5 concentration compartments of the first stage to an adjacent downstream stage,

and means for recovering purified liquid from the ion depletion compartments in a final downstream stage.

10 7. The apparatus of claim 6 wherein the width of said subcompartments is about 0.5 and 1.5 inches.

8. The apparatus of claim 6 wherein the thickness
of said subcompartment is between about 0.06 and 0.125
15 inches.

9. The apparatus of any one of claims 6, 7 or 8 which includes means in said concentration compartments for effecting turbulent flow of said second liquid.

20 10. The apparatus of any one of claims 6, 7 or 8 wherein the ion exchange material comprises a mixture of anion exchange resin beads and cation exchange resin beads and wherein the volume ratio of anion exchange
25 resin beads to cation exchange resin beads in said ion depletion compartments is between about 2.0 and 0.5.

11. The process for removing ions from a liquid which comprises passing a first liquid to be purified
30 through the depletion compartments of claim 1, passing a second liquid adapted to accept ions through said concentration compartments, passing an electrolyte through each of said anode and cathode compartments and recovering purified liquid from said ion depletion compartments.

12. The process of claim 11 wherein the ion exchange material comprises a mixture of anion exchange resin beads and cation exchange resin beads and wherein the volume ratio of anion exchange resin beads to cation exchange resin beads is controlled to be between about 1.75 and 1.25.

13. The process of any one of claims 11 or 12 wherein the voltage between a cell pair defined by an anion permeable membrane, a depleting cell, a cation permeable membrane and a concentration cell is between about 0.5 and 2 volts.

14. The process of any one of claims 11 or 12 wherein the flow velocity of liquid through said ion depletion compartments is between about 10cc/min/inch width and 300cc/min/inch width.

15. The process for removing ions from a liquid which comprises passing a first liquid to be purified sequentially through the depletion compartments in each stage of the apparatus of claim 6, passing a second liquid adapted to accept ions through the concentration compartments in each stage of the apparatus of claim 6, passing an electrolyte through each of said anode and cathode compartments in each stage of the apparatus of claim 6 and recovering purified liquid from the ion depletion compartments of said apparatus.

16. The process of any one of claims 11, 12, or 15 wherein the first liquid is treated in a preliminary step to remove ions and organics from said first liquid.

17. The process of any one of claims 11, 12 or 15 wherein the first liquid is treated in a preliminary step with an ion exchange resin to remove ions from said first liquid and with a scavenger resin to remove foulants from
5 said first liquid.

18. The process of any one of claims 11, 12 or 15 wherein the electrodeionization apparatus is beackwashed periodically by introducing cleansing liquid into the
10 apparatus of claim 1 into a normally used liquid outlet of each depletion compartment and removing said cleansing liquid from a normally used liquid inlet of each depletion compartment.

15 19. The process of any one of claims 11, 12 or 15 wherein the voltage in the electrodeionization apparatus is controlled to polarize water in the depletion compartments thereby to effect hydrogen ion transfer into the concentration compartments.

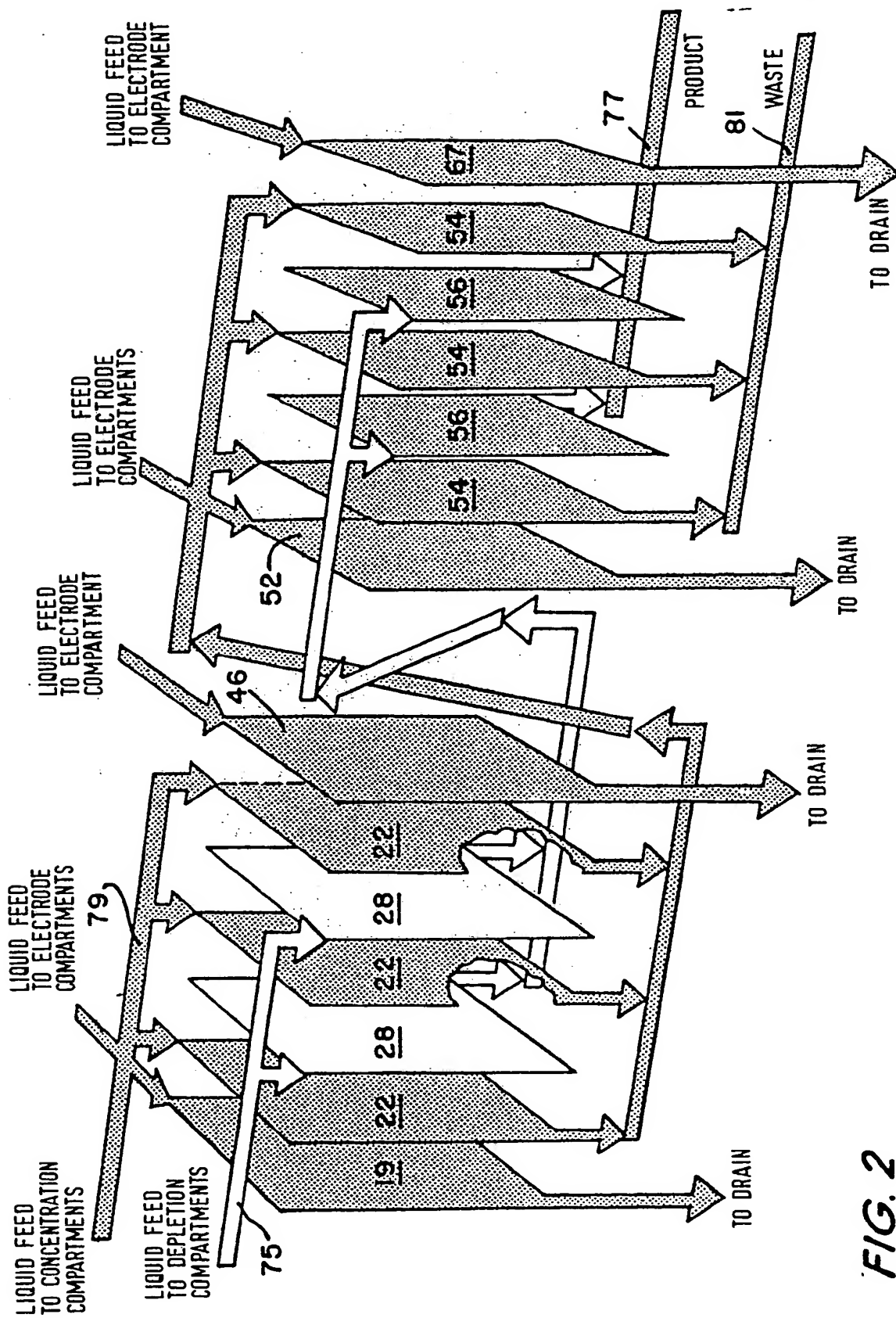
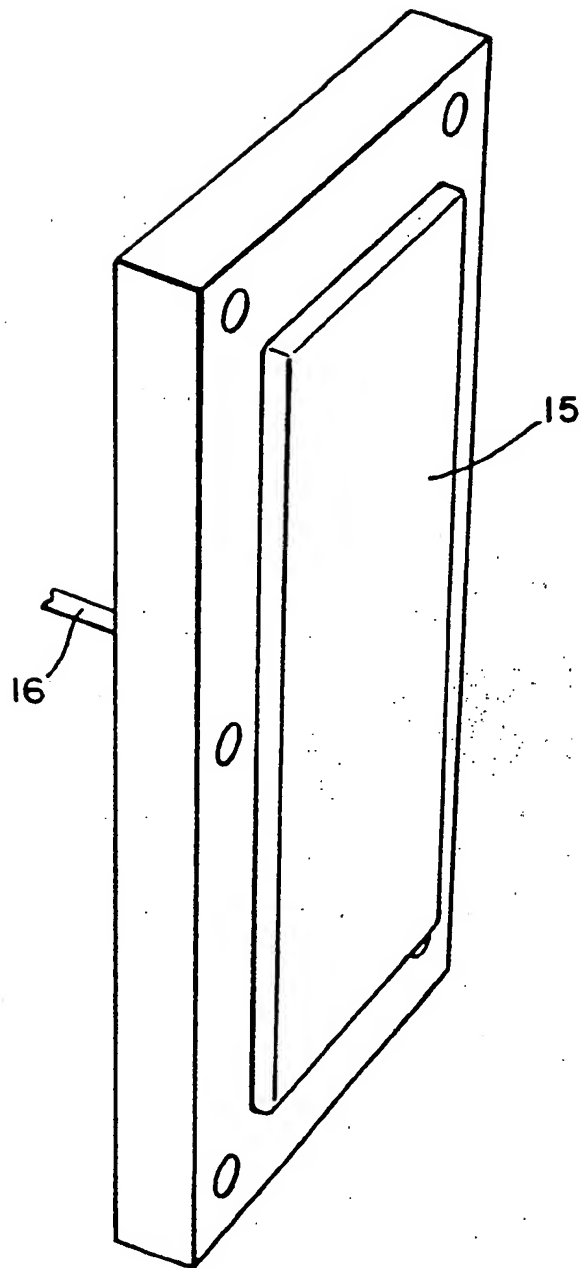
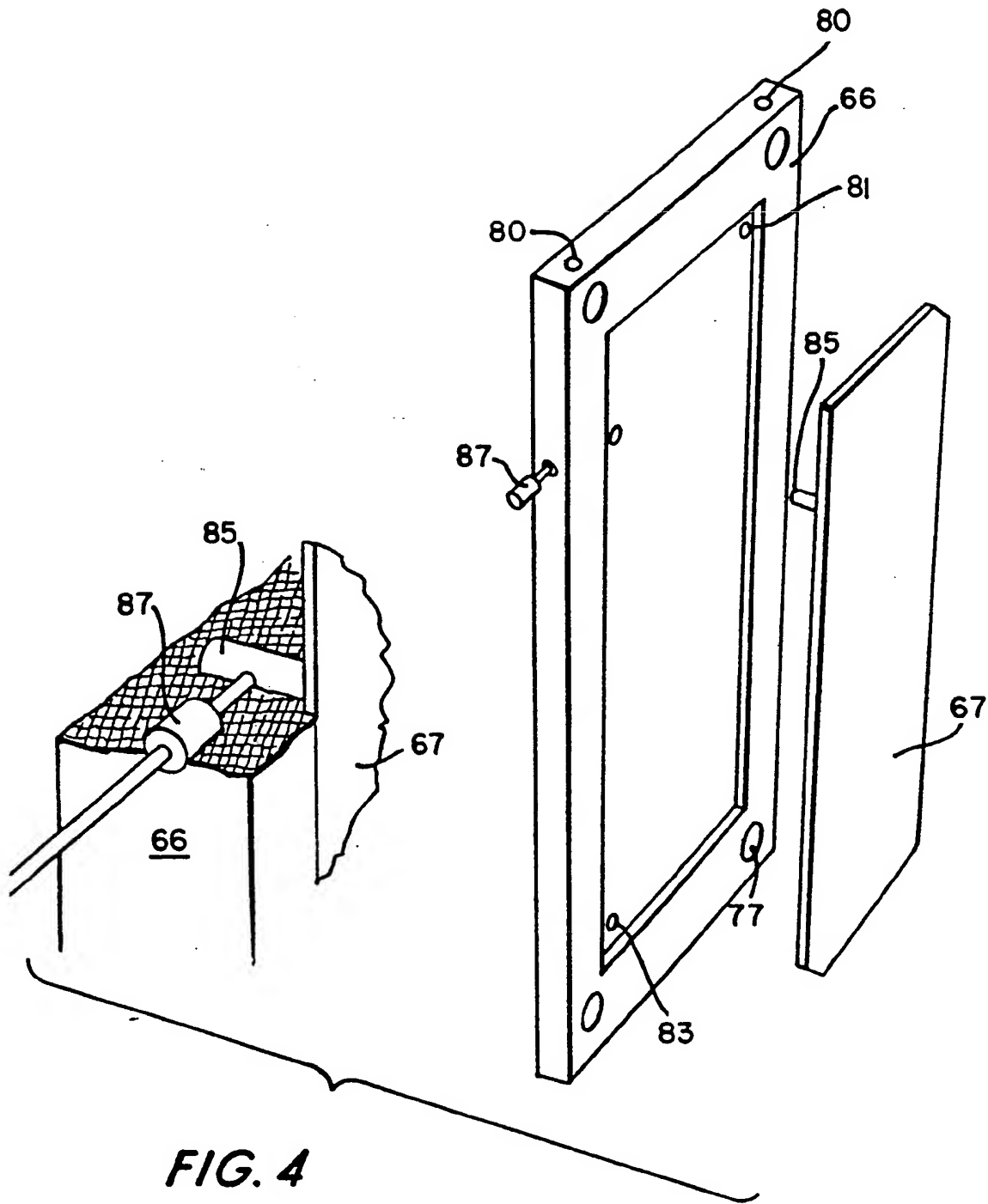
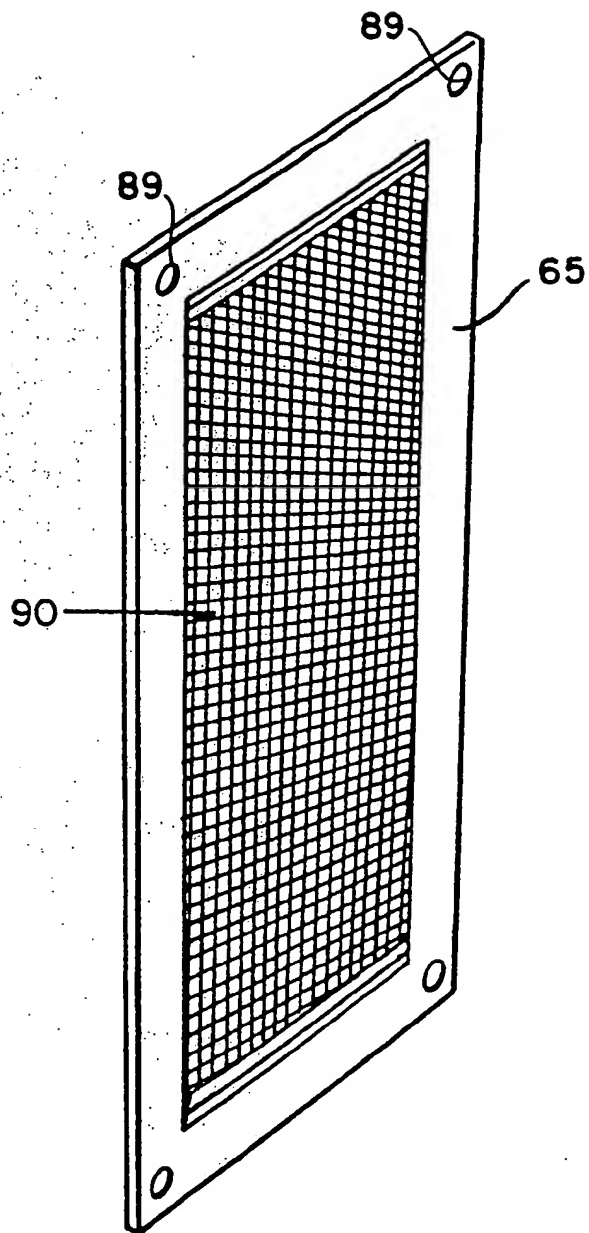


FIG. 2

**FIG. 3**



**FIG. 5**

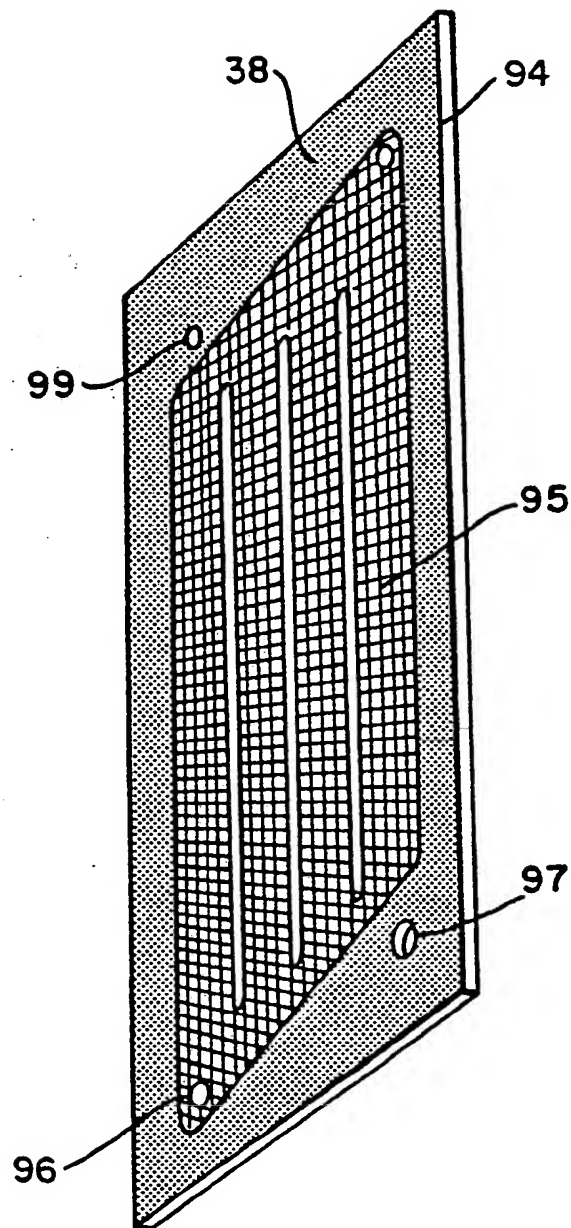
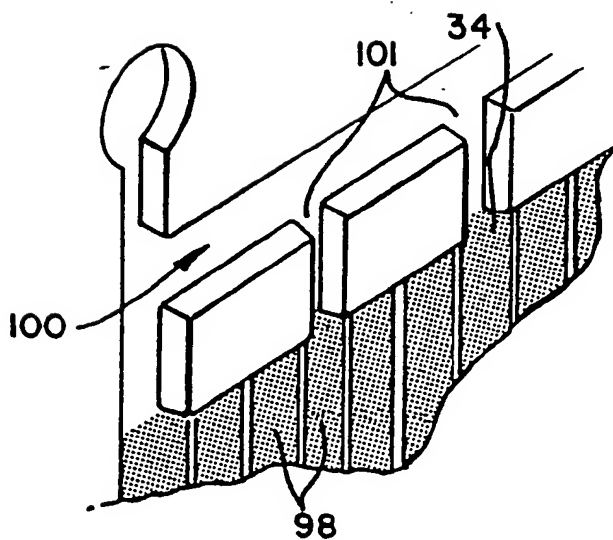
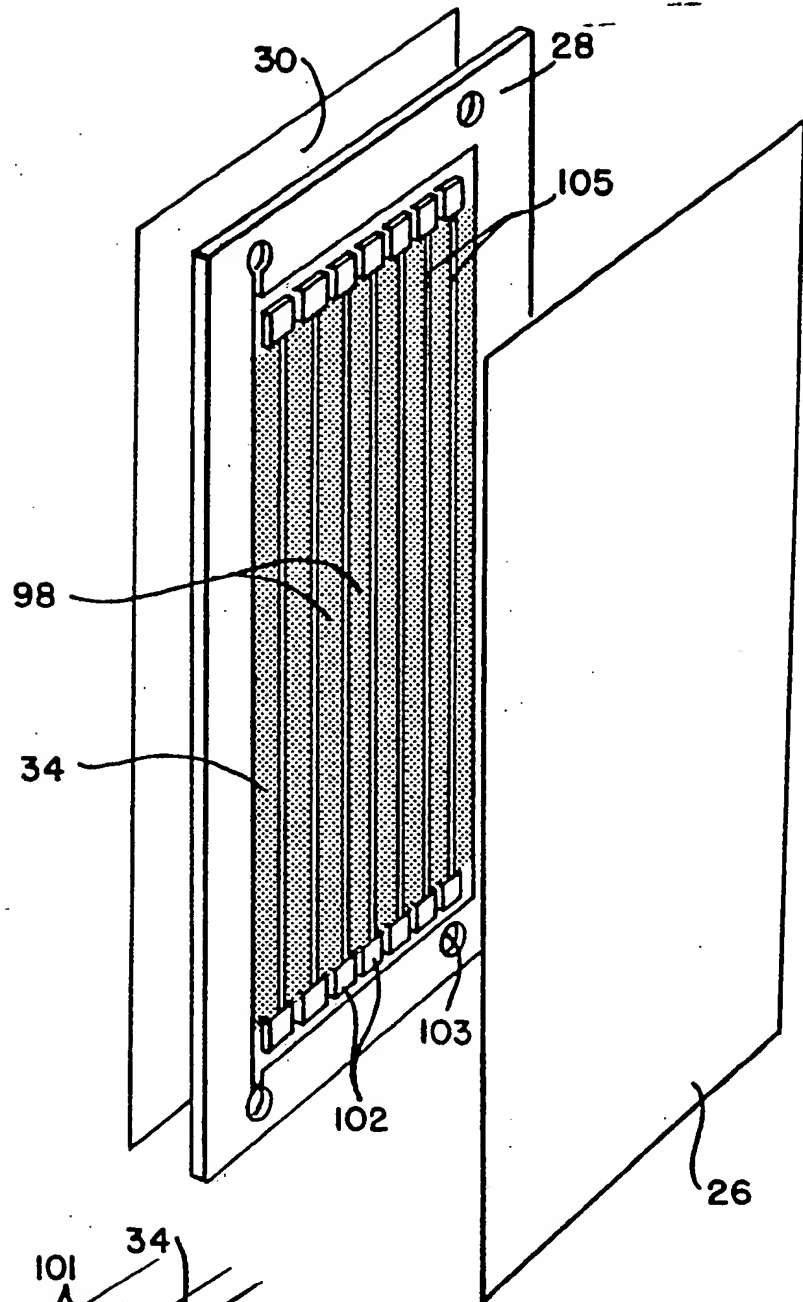
**FIG. 6**

FIG. 7**FIG. 8**

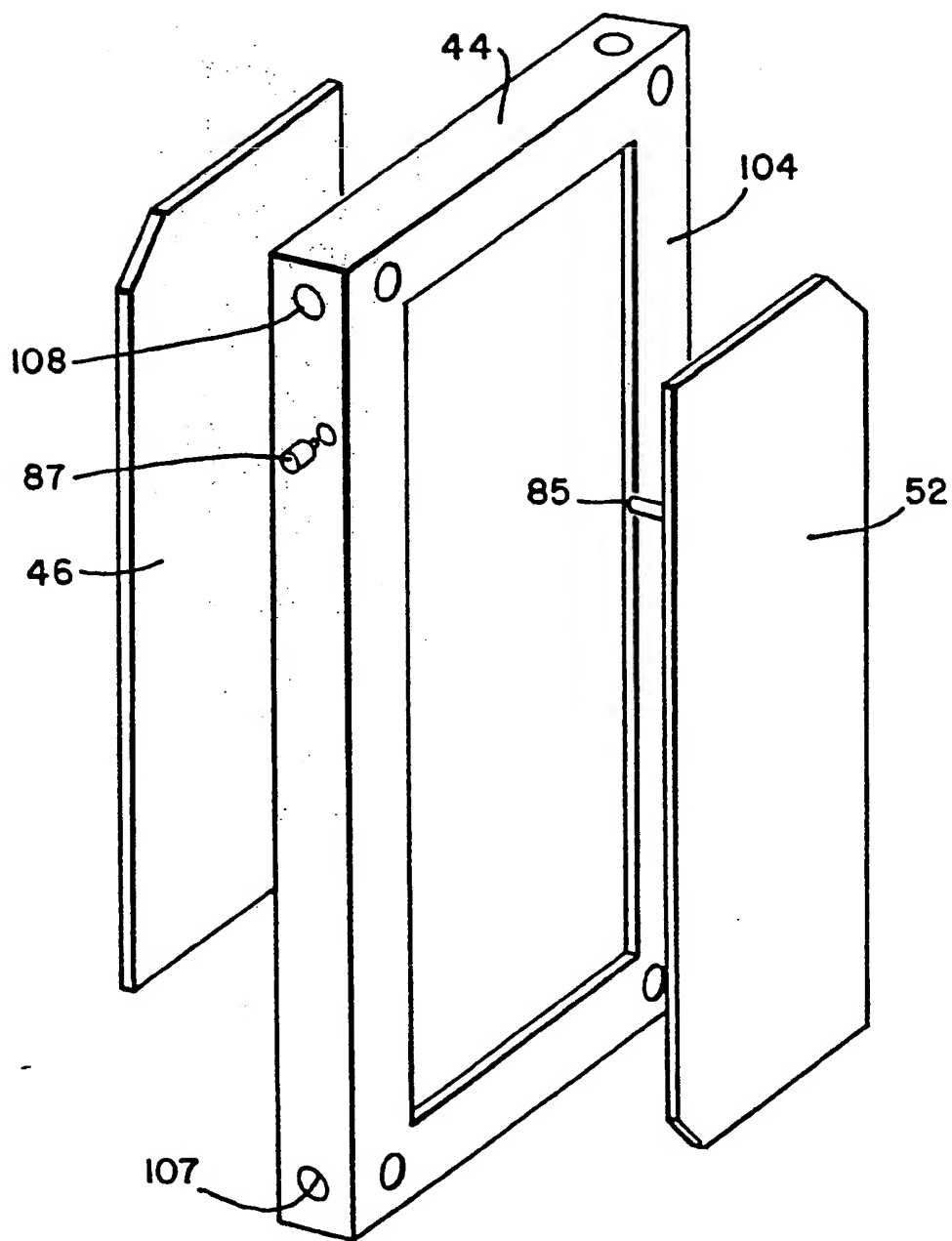
**FIG. 9**

FIG. 10a

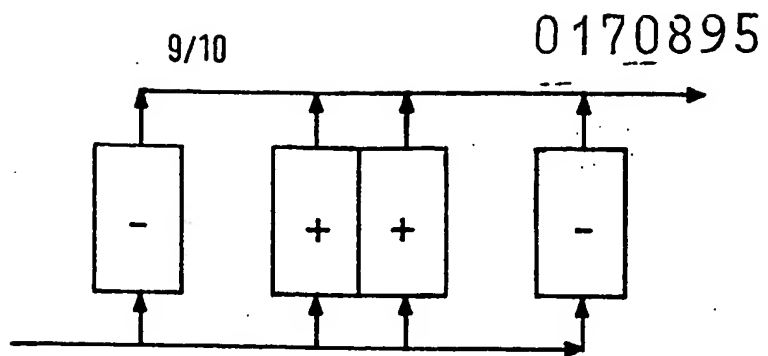


FIG. 10b

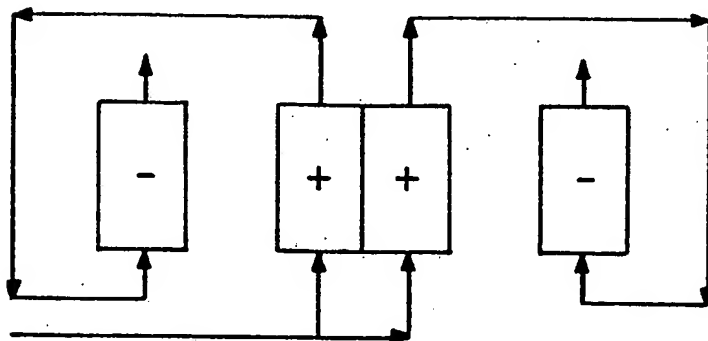


FIG. 10c

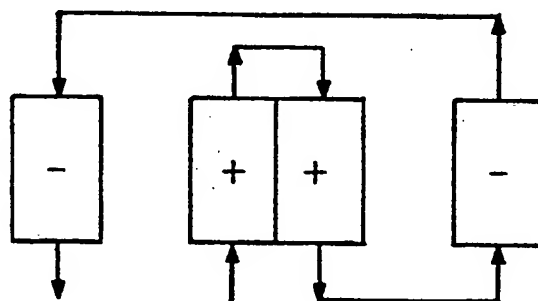


FIG. 10d

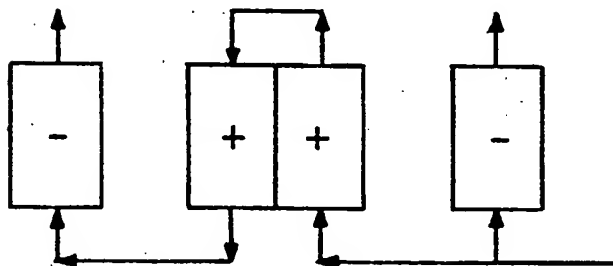


FIG. 10e

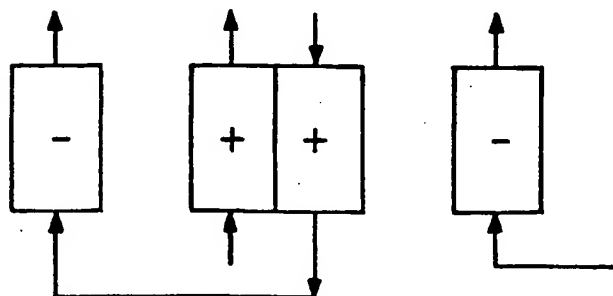
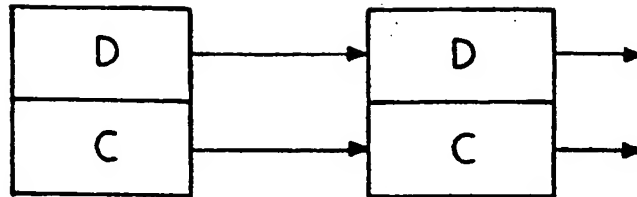
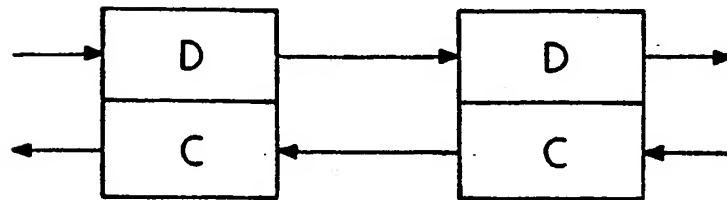
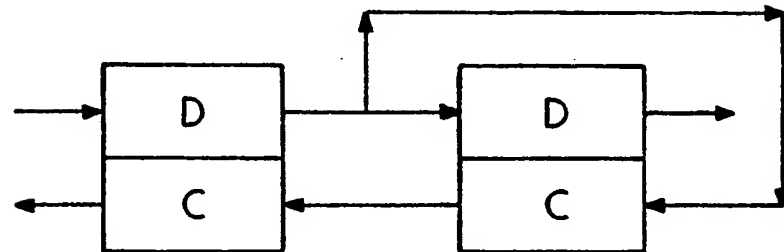
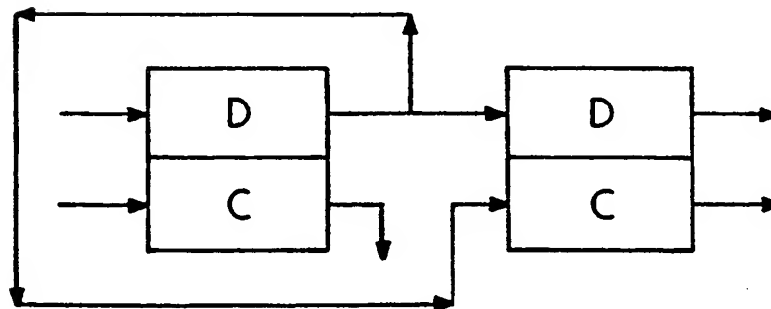
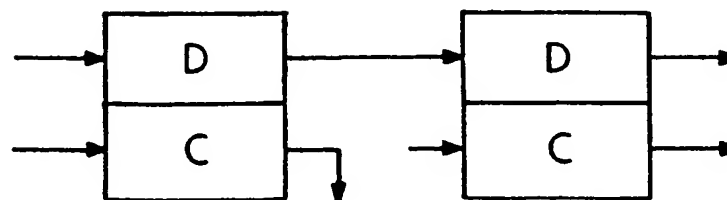


FIG. 11a*FIG. 11b**FIG. 11c**FIG. 11d**FIG. 11e*

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **85108378.2**

(51) Int. Cl.⁴: **B 01 D 13/02**
C 02 F 1/46, B 01 J 47/08

(22) Date of filing: **05.07.85**

(30) Priority: **09.07.84 US 828930**

(43) Date of publication of application:
12.02.86 Bulletin 86/7

(88) Date of deferred publication of search report: **08.10.86**

(84) Designated Contracting States:
CH DE FR GB LI NL SE

(71) Applicant: **MILLIPORE CORPORATION**
80 Ashby Road
Bedford Massachusetts 01730(US)

(72) Inventor: **Giuffrida, Anthony J.**
254 Chestnut Street
N. Andover, MA 01845(US)

(72) Inventor: **Jha, Anil D.**
13 Sheridan Street
Lexington, MA 02173(US)

(72) Inventor: **Ganzl, Gary C.**
74 Valleyfield Road
Lexington, MA 02173(US)

(74) Representative: **Henkel, Feller, Hänzel & Partner**
Möhlstrasse 37
D-8000 München 80(DE)

(54) Improved electrodeionization apparatus and method.

(57) An electrodeionization apparatus and process are provided for removing ions from liquids. Liquid to be purified is passed through depleting compartments containing mixed anion and cation exchange resin beads while a second liquid is passed through concentrating compartments free of ion exchange resin beads. Ions, under influence of a D.C. potential, pass from the depleting compartments into the concentrating compartments through ion permeable membranes. The beads in the depleting compartments are housed within subcompartments of controlled width and thickness and are retained therein by the ion permeable membranes which are secured to the walls of the subcompartments.

EP 0 170 895 A3



European Patent
Office

EUROPEAN SEARCH REPORT

0170895

Application number

EP 85 10 8378

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
D, Y	US-A-3 291 713 (E.J. PARSI) * Column 3, lines 3-16; column 4, line 36 - column 5, line 8, example 4; figure 3 *	1, 5, 6, 10-12, 15	B 01 D 13/02 C 02 F 1/46 B 01 J 47/08
A	---	16, 17, 19	
Y	GB-A- 877 239 (THE PERMUTIT CO. LTD.) * Claims 1, 7; page 2, lines 56-61; page 1, line 84 - page 2, line 5 *	1, 5, 6, 10-12, 15	
A	DE-A-3 238 280 (H.W. LIEBER) * Figures 2, 4, 7, 8; claim 7; page 12, lines 10-16 *	1, 4, 9	TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
A	DE-A-1 792 301 (P. KOLLSMAN) * Figure 4; page 7, lines 15-22; example 1 *	1, 5, 6, 10-12, 14, 15	B 01 D B 01 J C 02 F
D, A	US-A-3 384 568 (M. KATO et al.) --- -/-	1, 6, 11 , 15	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 31-07-1986	Examiner CECCHINI
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO Form 1503 (3/82)



European Patent
Office

EUROPEAN SEARCH REPORT

01-70895
Application number

EP 85 10 8378

Page 2

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	GB-A-1 013 307 (IONICS INC.) -----	1, 5, 6, 10-12, 15-17, 19	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 31-07-1986	Examiner CECCHINI
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

THIS PAGE BLANK (USPTO)